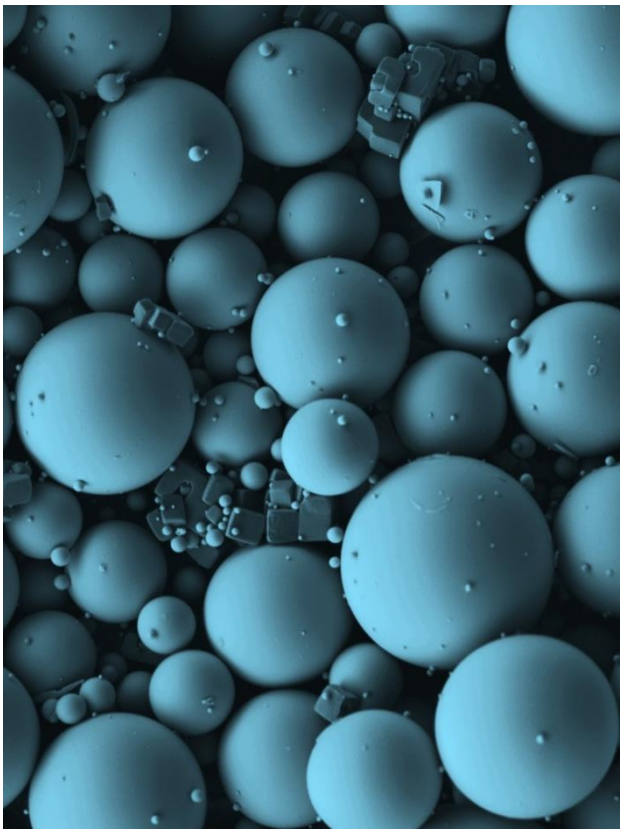

BOOK OF ABSTRACTS

Processing and Properties of Advanced Ceramics and Glass

Workshop

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CONTENT

Stability of photosensitive zirconia suspensions as a substantive factor for rheological measurements

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ABSTRACT

The stability of suspensions is a key factor not only for determining the dynamic viscosity and rheological behavior of ceramic suspensions, but also for their practical applications - especially when shaping ceramic bodies. The stability of the suspension is particularly important in DLP (Digital Light Processing) and SLA (Stereolithography) 3D methods of producing green bodies, when instability and sedimentation of the suspension would lead to the formation of defects or unsuccessful printing [1]. Often used and straightforward method for measuring sedimentation and thus the inhomogeneity of the suspension is the measurement of the level of sedimentation in a cylinder. However, this method is not standardized - neither the length of the entire measurement, nor the measurement time intervals [2].

Suspensions containing two types of zirconia nanopowders (CY3Z-RS and CY8Z-RS, both with d_{50} = 300 nm) and acrylate resins (Flex and Tough) were prepared. The prepared suspensions (with a volume filling of 0 - 40 vol.%) were subjected to a rheological measurement (time sweep) for the creation of a new, semi-empirical model for ceramic suspensions. However, how is it possible to qualitatively verify that the prepared suspensions for rheological measurements were stable and that there was no phase separation or sedimentation during the measurement?

A very accurate identification of the stability of zirconia suspensions can be performed using the LUMiSizer analytical centrifuge (Malvern Panalytical). During sedimentation analysis, near-infrared light transmission over the total length of the cell containing the dispersion is automatically determined and the time development of these transmittance sedimentation profiles is also recorded. These data can be used to determine the instability index, which is a dimensionless number between 0 and 1 (where the value of 0 corresponds to a stable system without sedimentation and the value equal to 1 corresponds to the complete segregation of phases). All measured suspensions achieved an instability index below 0.05, which emphasized their high kinetic stability. The instability index slightly decreased with an increasing volume percentage of zirconia, thus the stability of the suspension partially increased. The stability analysis proved that all measured suspensions in the entire studied concentration range can be considered kinetically stable over time.

Keywords: instability index, LUMiSizer device, oxide ceramics, zirconia nanopowders

Acknowledgment: This work has been supported by the project of Specific Research by the Ministry of Education, Youth and Sports of Czech Republic FCH-S-24-8592.

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Optimization Strategy for Debinding of Composite Ceramic Material Produced by 3D Printing

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ABSTRACT

Fused Filament Fabrication of Ceramics (FFFC) is an innovative additive manufacturing technique for producing complex ceramic structures. This method enables the creation of complex shapes that are difficult to achieve using traditional ceramic forming techniques. In addition to professional applications, it has the potential to be a user-friendly approach for hobby users as well [1].

It is important to produce structures with minimal defects, such as cracks, delamination, and non-uniform shrinkage. To maintain the shape of the manufactured object and prevent defects, controlling both the printing process and debinding conditions is crucial [2]. The thermal debinding process involves removing of the polymer matrix along with other volatile components like dispersants or plasticizers. To make the debinding process more reliable, it's essential to optimize and experimentally determine suitable heating conditions that work with common technologies and equipment, especially for users who don't have access to specialized furnaces.

This work focuses on optimizing the debinding process for composite mullite-based ceramic materials to obtain uniform, defect-free samples, ideally using non-specialized equipment. Square-shaped and cylindrical samples of various dimensions were manufactured using FFFC technology on a commercial Ender 5-Pro FFF printer with a 0.4 mm nozzle. The samples were exposed to various thermal processing regimes to obtain information about limitations in debinding process of studied composite ceramic system. Optical microscopy was used to examine the samples after the debinding process. Thermal processing regimes were optimized based on the shape and dimensions of the samples.

Keywords: Composite Ceramic Material, Debinding process, Fused Filament Fabrication of Ceramics

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Al doped ZnO by sol-gel dip-coating method

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ABSTRACT

Over time, ZnO has received broad attention due to its interesting properties, such as exciton binding energy of 60 meV, a band gap energy of 3.37 eV and electron mobility value around 1 to 200 $cm^2V^{-1}s^{-1}$, ZnO is a well-known transition metal oxide preferred for various applications including optoelectronics, sensor layer, solar cells, and protective coatings [1,2].

Metal doping, specifically by the II, III, and IV group elements, can enhance the properties of ZnO films. Group III elements like B, Al, Ga, and In are used as extrinsic donors of free electrons through the substitution of a trivalent ion (M^{3+}) for the zinc cation, resulting in a higher conductivity and better transparency for the doped films [1]. Among them, Al-doped ZnO (AZO) is favourable in terms of easy fabrication and cheap raw materials. In this study, we prepared and investigated ZnO thin films with different amounts of solvent (ethanol) and series of Al doped ZnO (ZnO : Al) films with different Al concentrations deposited on glass substrates using the sol–gel dip coating technique. The XRD results confirmed formation of hexagonal wurtzite crystal structure of ZnO films with the presence of reflections peaks of the planes from wurtzite ZnO structure. Microstrain and dislocation density evaluations on ZnO film (15%E) showed the values of 10.13 $\mu m.m^{-1}$ and 6.87 nm^{-2}, respectively. Using UV-vis absorption data and Tauc plot, the band gap energy value of ZnO was estimated as 3.28 eV. The surface chemistry of ZnO film (15%E) and AZO with 6% of Al dopant were analysed by XPS. SEM images taken from the top and cross-section revealed the particle size and thickness of the films as ~70 nm and ~200 nm, respectively. These preliminary results will be used for the synthesis, characterization, and evaluation of Nitrogen doped AZO thin films according to the work plan of the thesis.

Keywords: TCO, AZO, sol-gel, dip coating.

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This project has received funding from the European Union´s Horizon 2020 research and innovation programme under grant agreement No 739566.
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Characterization, functionalization, and improvement of glasses for pharma using combined plasma and ion-exchange treatments (P-IET)

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ABSTRACT

Borosilicate glass is used worldwide for pharma packaging, but it still can be improved to prevent surface organic contaminations, breakage, corrosion, and delamination that might compromise the drug quality, safety, and efficacy. This study implements an effective and economical strategy combining plasma and ion-exchange treatments (P-IET) of borosilicate medical glass vials (MGVs) to enhance their surface cleanliness, mechanical characteristics, and chemical durability without compromising glass transparency and product quality. Utilizing KNO_3 molten salt bath, an ion exchange treatment was conducted at 450°C and 500°C for 2, 12, and 24 hours, preceded by the application of air/Ar of cold plasma treatment for 5-10 seconds. The mechanical properties of treated vials were characterized by Vickers indentation, and mechanical crushing load measurement. The chemical stability assessments through ion leaching tests in different pH environments under normal conditions were also performed. Raman spectroscopy, and a 3D confocal microscope were respectively used to detect variations in surface structure and roughness.

The P-IET effectively prevented the formation of radial cracks after Vickers indentation. The crushing loads for full-body vials after P-IET treatment at 450°C for 2, 12, and 24 hours (≈1275 ± 50, 1613 ± 50, and 1775 ± 70 N, respectively) and at 500°C for the same durations (≈1493 ± 31, 1945 ± 51, and 2124 ± 21 N) increased significantly. EDS and XPS analyses confirmed reduced sodium profiles and increased potassium concentration near the surface. Raman spectra showed noticeable shifts, particularly in the Q_n species region, with increasing Q_3 and decreasing Q_2 and Q_4 concentrations in the treated MGVs. Normalized *ICP-MS* data indicated lower release of potassium (K) and sodium (Na) from treated MGVs in various extraction solutions after 1 and 6 months under normal conditions, confirming delayed glass dissolution through ion exchange or hydrolysis mechanisms. Overall, the study suggests that P-IET can improve properties of borosilicate MGVs, addressing concerns in the pharmaceutical industry regarding MGVs surface contamination, sterilization, fragility, and potential drug quality compromise using relatively economical, straightforward, and accessible techniques.

Keywords: Glass vials, chemical durability, ion-exchange process, roughness, plasma treatment.

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Utilisation of alkali-activated waste glass for developing porous glass ceramics

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ABSTRACT

Waste glass can be effectively utilized through reaction with alkali to produce useful material used in construction industries, reducing the high environmental impact of building materials production. The selection of the alkali concentration and type, including the synthesis method during activation, is crucial in modifying the chemical and physical characteristics of the final product, particularly when subjected to thermal treatment. [1]. In this study, waste fiberglass was activated using high-molarity (8M) NaOH and low-molarity (3M) NaOH or KOH, where 20 wt% corroded AZS refractory was added to enhance mechanical and thermal properties. The resulting paste was cured at 60°C for 24 hours in an electric oven.

After alkali dissolution, FTIR and XRD results confirmed the presence of hydrated alkali aluminosilicates and alkali carbonates. 8M NaOH activation resulted in 4 times higher compressive strength than 3M activated samples. However, upon thermal at temperatures ranging from 800-1000°C with a heating rate of 5°C/min and a 1-hour dwell time, the 8M activated samples showed cracks and dimensional instability. Low molarity activated samples developed into porous glass ceramics. Specifically, NaOH-activated porous glass ceramics with porosity up to 87% and a density range of 0.4-0.9g/cm^3 were obtained, which can be applicable as lightweight aggregates or thermal and acoustic insulation. KOH-activated samples displayed dense glass ceramics (35-42% porosity and density 1.5-1.7g/cm^3) with low shrinkage and high dimensional stability. The fired KOH-activated samples have similar porosity and compressive strength (23-32MPa) but reduced density compared to commercially available facing bricks [2]. 8M activated samples showed much better resistance when exposed to an acidic environment, making them suitable for acid-resistance applications.

Keywords: alkali activation, porous glass ceramic, waste glass, upcycling.

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Electrochemical performance of graphite and graphite-silicon anodes coated with atomic layer deposited ZnO in Li-ion batteries

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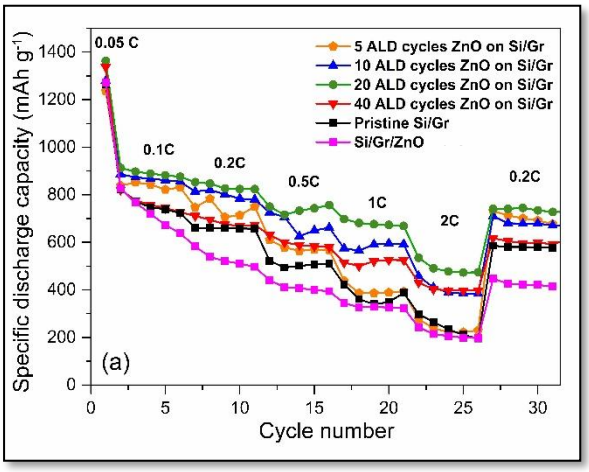
ABSTRACT

Graphite (Gr) is a widely-used anode material for Li-ion batteries with a specific capacity of 372 mAh g^{-1}. ZnO, with its higher theoretical capacity of 978 mAh g^{-1}, presents a viable option for high-energy demand applications. However, the use of bare/bulk ZnO is limited by relatively high volumetric expansion/shrinkage during cycling. To address these challenges, Gr/ZnO composite anodes were produced via atomic layer deposition (ALD). Anodes were prepared from ball-milled graphite, conductive carbon, and sulfonated alginate binder in an 80:10:10 weight ratio. ZnO films were deposited through ALD at 100 °C using diethyl zinc and deionized water as precursor and reactant, respectively. Various number of ALD cycles (10, 20, and 40) were performed to achieve different ZnO layer thicknesses. Evolution of the ZnO layers on graphite anodes was observed through scanning electron microscopy, X-ray photoelectron spectroscopy. Electrochemical performance was assessed through rate capability and long cycle tests within a Li/Li^+ voltage window of 0.01-1.5 V. Differential capacity analysis (d*Q*/d*V*) elucidated decay properties and contributions of each material to total capacities. Similar processing and characterisation was performed also on graphite-silicon anodes coated with ALD ZnO nanolayer. The results demonstrate the successful enhancement of anode performance through ALD assisted Gr/ZnO or Gr-Si/ZnO composites, offering promising implications for the advancement of Li-ion battery technology.



Keywords: Li-ion battery, anode, atomic layer deposition, ZnO, electrochemical performance

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How glass composition changes alkali ion diffusion in soda lime glass?

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ABSTRACT

While the effect of the chemical composition on the diffusion of alkali cations in silicate glasses is well-known, the influence of compositional changes resulting from Na^+/K^+ ion exchange on the diffusion of alkali ions in silicate glasses is still unclear. The present work aims to investigate whether the structural changes of glass because of Na^+/K+ ion exchange have any significant impact on the mobility of Na^+ and K^+ in alkali-lime silicate glasses.

Alkali-lime silicate glasses with the nominal composition $(15\text{-}X)Na_2O{\cdot}XK_2O{\cdot}10CaO{\cdot}75SiO_2$, where X varies from 0 to 15, were prepared using the melt-quench technique. The synthesized glasses were characterized in terms of their density, glass transition temperature (Tg), and softening point (Ts). Subsequently, the glasses were subjected to Na^+/K^+ ion exchange using molten salt method (KNO_3) at various temperatures, from 430°C to 470°C, for 4 hours. The surface chemical composition and potassium diffusion coefficient of the ion-exchange modified glasses were analyzed using energy-dispersive X-ray spectroscopy (EDXS). Additionally, the structural changes of glasses during Na^+/K^+ ion exchange were examined using micro-Raman spectroscopy.

The physical properties, e.g., Tg and density, and the structure of glasses produced by the melt-quench method followed the behavior predicted by mixed alkali effect (MAE). In contrast, a significant deviation from the expected behavior by MAE was observed in the case of glasses subjected to Na^+/K^+ ion exchange. Micro-Raman analysis showed that the modification of the glass network, as indicated by the $I(Q^3)/I(Q^2 + Q^4)$ ratio, is responsible for the observed deviation. The implications of alkali ion mobility in ion-exchanged glasses for applications such as batteries and energy storage are critically discussed.

Keywords: Mixed alkali effect, ion mobility, micro–Raman Spectroscopy, soda lime silicate glass

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Physicochemical properties of barium crystal glass

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ABSTRACT

15 different glass compositions were derived from the base glass barium crystal glass. Glass compositions were adjusted by changing the amount of each oxide. The glass batches were prepared at a temperature range of 1500 to 1600°C in an ambient atmosphere. The amorphous character of all samples was determined using X-ray diffraction analysis. The inductively coupled plasma optical emission spectroscopy was used to study the chemical composition of the glasses after their dissolution in the mixture of HF and $HClO_4$.
The density of all glass-forming melts was measured using the Archimedes principle. All studied melts showed a linear density-temperature dependence. The surface tension of all samples was measured using sessile drop profile analysis. The surface tension was determined over the 1100-1400 °C temperature range. The drop profiles recorded at 1190°C were analyzed by the numerical integration of Laplace's equation using the experimentally determined melt density. For the comparison, the drop profiles were also evaluated using Dorsey's approximate method [1,2]. The calculated data are in good agreement with the experimental values (Fig. 1). It was found that the surface tension is significantly decreased by increasing the content of K_2O, ZnO, Al_2O_3, and SiO_2.

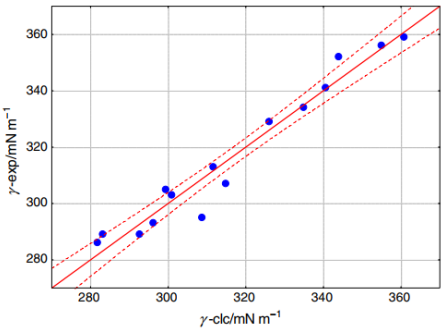

Fig. 1: Experimental and calculated values of surface tension (points). The dotted lines represent the 95% confidence limit.

Keywords: Sessile drop, Surface tension, Dorsey method, Glass melt, Density of melts.

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Use of a Fluidized Glass Bead Bed for Rapid Charring of Wood Surfaces

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ABSTRACT

Although wood has been used as a construction material since the beginning of human existence, addressing its inherent deficiencies remains a major challenge. Wood changes its dimensions with changing moisture content, decomposes by a wide variety of organisms, burns, or is degraded by ultraviolet energy. To overcome these, many methods of chemical modification of wood itself have been proposed, i.e., treatments other than standard wood coating or finishing. These methods involve chemicals such as acetic, butyric, phthalic, succinic, maleic, propionic, and butyric anhydride, acid chlorides, etc., many of which are toxic or corrosive chemicals that can harm the environment [1]. Thermal treatment, represents a significantly less environmentally problematic approach. In principle, wood is exposed to temperatures between 180 and 250°C in an atmosphere with a low oxygen content to avoid wood combustion reactions. Depending on a particular thermal treatment, different types of thermally modified timber (TMT) are available on the market today. All of them exhibit improved weather and biological resistance. However, TMT suffers from decreased mechanical properties: lower bending and shear strengths or more brittle behavior. The mechanical declination arises from a weakening of structural integrity within the volume of TMT due to thermal degradation of its components [3]. With this respect, limiting the thermal modification only to the surface of the wood piece represents a good compromise, allowing for sufficient protection of the wood surface without sacrificing the internal wood mechanical properties of the wood. The method of surface charring by naked flame is traditionally used in Japan (*yakisugi*), or in Europe to preserve vineyard wood posts buried in the soil. Alternately, the controlled heat load can be applied by a hot plate [4] or electrical discharge [5]. A common technical limitation of these methods is a requirement for a well-defined flat surface of wood piece, and an impossibility to charr/carbonize the entire wood surface circumference in a single step. This contribution evaluates the possibilities and results of using a fluidized powder bed of glass beads heated to temperatures above 200 °C to enable uniform surface charring of beech wood (*Fagus sylvatica L.).* Consequently, an attention is paid to the issue of selecting a suitable glass or ceramic powder material that will enable RF and/or microwave heating of the fluidized bed.

Keywords: charring, fluidized bed, glass beads, pyrolysis, wood.

Acknowledgment: This research has been supported by the Czech Science Foundation (GAČR), project No. 24-10430S.

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Nd^{3+} ion doped oxyfluoride silicate glasses and glass-ceramics for NIR laser application

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ABSTRACT

Rare-earth (RE) doped $NaYF_4$ Oxyfluoride Glass Ceramics (OxGCs) is one of the most efficient hosts for RE ions due to its low phonon energy that increases the luminescence while properties preserving the excellent mechanical properties of the parent glasses. It has two crystalline forms, cubic and hexagonal, which can be changed with each other by setting the glass composition and/or heat treatment conditions. This ability to adjust the crystal phase allows for the selection of settings to obtain the most optically favourable hexagonal phase possible. Thus, the development of RE-doped $NaYF_4$ GCs, as well as the RE content effects on the crystal precipitation and its structural optical properties, are worth investigating. Here, (0.2-1.0) NdF_3 doped $NaYF_4$ OxGCs (mol%) were prepared by melt-quenching followed by controlled crystallization of the parent glass. Structural properties were analyzed to confirm the hexagonal phase precipitation and incorporation of Nd ions in this phase. The absorption shows an increment with the NdF_3 content in the GCs. However, the NIR emissions show an enhancement up to 0.5 mol% of doping, decreasing at higher concentrations. Fluorescence lifetimes follow the same behavior, indicating the optimum Nd^{3+} content for emission efficiency. According to the extremely strong emission band at 1056 nm and the evolution of the optical properties, such as the high stimulated emission cross-section and branching ratio obtained for transitions in the NIR region at around 1000-1100 nm, the $0.5NdF_3$ doped GCs can be considered as a promising material for NIR laser applications.

Keywords: RE-doped $NaYF_4$ Oxyfluoride Glass Ceramics; optical properties; NIR laser applications.

Acknowledgment:

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Modification of Si_3N_4 – Y_2O_3 composites – conditions of oxyacetylene torch and its optimisation

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ABSTRACT

Dense Si_3N_4 with the addition of rare earths oxide (in this case Y_2O_3) by FAST (rapid hot pressing) at 1700 °C and 50 MPa pressure for 7 min were prepared. Yttria as sintering additive was chosen because of the oxidation resistance of silicon nitride with this addition at high temperatures. Surface of the ceramic substrate was modified by oxyacetylene flame by means of formation of protective layer on the surface composed from yttrium silicate. The character of affected area and surface morphology was studied in dependence: of the reached temperature on the surface of substrate, the dwell time on the annealing temperature, gas flow rate and the ratio of oxygen /acetylene gases. Finally, the influence of these parameters on the degree of oxidation of surface layer, thickness, porosity and phase composition will be evaluated.

Keywords: rare earths oxides, silicon nitride, oxyacetylene flame

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The influence of phosphor crystallinity on the optical properties of PiG

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ABSTRACT

Recently, rapid advances in high-power and high-brightness LED lighting technology have been achieved. To address the issue of yellowing that occurs when epoxy-LEDs are exposed to UV light, glass is now being utilized to encapsulate the phosphor instead of epoxy resin. The phosphor in glass (PIG) offers excellent thermal durability, chemical stability, and a tunable refractive index inherent to glass. The yttrium aluminium garnet - YAG is typically employed as a host for phosphor, possessing a refractive index of 1.83. Consequently, numerous investigations of the glass matrix have been undertaken to adjust the refractive index of the embedding glass to match that of the phosphor to improve the optical properties of the final composite[1, 2].
In the previous research, a novel YAG:xEu_2O_3 (x = 0.125–0.750) phosphor in the shape of microspheres was synthesized by the modified sol-gel Pechini method and flame synthesis [3]. In the present study, these microspheres with different degrees of crystallinity (amorphous, partially crystallized and fully crystallized) are embedded into the following glass matrices with different refractive indexes:

1. 11.4SiO_2-24.3B_2O_3-35ZnO-5.3Li_2O-12La_2O_3-12WO_3 (M1, RI = 1.8)
2. 10Bi_2O_3-40ZnO-50B_2O_3 (M2, RI = 1.73)
3. 14.1SiO_2-30.1B_2O_3-43.2ZnO-6.6Li_2O-3La_2O_3-3WO_3 (M3, RI = 1.67)

TG/DTA analysis was used to determine the glass transition and crystallization temperatures of the fabricated glass matrices and microspheres, which are crucial factors for viscous flow sintering. The optical characteristics of the composites after sintering in viscous flow were evaluated. The degree of crystallinity directly impacts the density of microspheres and, consequently, their refractive index.

Keywords: PiG, refractive index, viscous flow, YAG phosphor

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Design and manufacturing of SOFC components by 3D printing technology

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ABSTRACT

Solid Oxide Fuel Cells (SOFCs) are environmentally efficient energy conversion devices based on functional ceramics, but the complicated fabrication procedure partially limits their application. 3D printing methods have widened the scope for designing more performing microstructures for SOFCs, providing material savings, high production efficiency, and low cost [1]. However, the advancement and adoption of 3D printing as an alternative manufacturing technology requires to improve in all aspects of 3D-printing technology, slurry preparation process optimization, debinding, and sintering process. Among the 3D printing technologies, direct ink writing (DIW) is a simple and low-cost method for rapid manufacturing of ceramics in complex geometries [2]. The study aims to develop self-supported electrolytes based on 8 mol% yttria-stabilized zirconia using DIW. The ceramic inks with 75.2 wt% of solid loading and appropriate rheological properties were formulated. The green bodies with various infill patterns were printed with a nozzle with diameter of 0.4 mm and sintered in the temperature range of 1450-1550°C in air. The physical and mechanical properties of sintered samples were determined. After sintering, the printed samples showed uniform densification and grain size distribution. The surface displayed concentric and corrugated patterns resulting from different infilling setup. The concentric and corrugated electrolytes had average thicknesses of approximately 0.25 mm and 0.17 mm, respectively. Biaxial strength testing revealed that the flexural strength of the ceramic electrolytes was approximately 580 MPa, regardless of the surface type. This strength is sufficient [3] for self-supported structures, making extrusion-based DIW 3D printing a viable option for fabricating high-quality self-supported electrolytes for SOFC.

Keywords: 8YSZ, SOFCs, Direct ink writing 3D printing, rheology, flexural strength

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Fabrication of Complex-shaped Translucent Glass Structures by Digital Light Processing

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ABSTRACT

Glass 3D printing offers several advantages, including the ability to produce intricate and highly precise glass designs and prototypes. This technology enables artists, designers, and manufacturers to explore innovative applications in diverse fields such as architecture, art, and industrial design. Several attempts have been made to manufacture transparent glass parts by various additive manufacturing techniques [1]. However, during the viscous flow sintering of the 3D printed green parts, the problem occurs in achieving transparency of the final products [2]. The current work optimized slurry formation and sintering parameters to address this issue. The tableware glass in the Barium crystallin system was crushed, milled, and sieved to obtain glass powder with a particle size of less than 40 µm. A slurry was created by mixing 57% glass powder, 38% photocurable resin, and 5% polyethylene glycol. Using digital light processing technique, green parts in a gyroid shape (1x1x1cm3) were printed with a layer thickness of 50 µm.
Based on thermogravimetry and hot stage experiments the green objects were subjected to a three-stage heat treatment process: 1) heating to 400ºC at a rate of 0.2ºC/min and holding for 5 hours; 2) heating to 500ºC at a rate of 0.5ºC/min, holding for 3 hours, then heating to 700ºC at a rate of 10ºC/min and holding for 1 hour. X-ray diffraction analysis confirmed the amorphous nature of the final sintered scaffolds. The final quality of sintered samples was analyzed by scanning electron microscopy.

Keywords: Stereolithography Additive Manufacturing, Viscous Flow Sintering, Translucency.

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Development of glass filaments for FFF additive manufacturing: challenges and failures

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ABSTRACT

The development of novel materials has advanced significantly in recent years, especially for Fused Filament Fabrication of Ceramic parts (FFFC). The key advancements can be considered for: 1. Material Development, 2. Print Quality and Resolution, 3. Post-Processing Techniques, 4. Hybrid Manufacturing Approaches and 5. Applications in Industry. Despite the progress achieved, new challenges remain mainly in the areas of materials availability that were not yet used as accessible for the FFF printing technology. This study focused on the development of new composite material for fused filament fabrication of glass (FFFG) and glass-based structures including the verification of their printability and application limitations. Recycled glass powder as an important inorganic silicate material was selected due to environmental consideration. It is an inexpensive material that can find new application areas, due to its many advantages such as mechanical properties, chemical and heat resistance and the possibility of producing glass components with arbitrary and complex geometries. After production of a novel filament composition, it is crucial to optimize both the material load content and their physical-chemical properties. In the first stage we used the load of inorganic particles at the level of 65w/w% that were combined with two component thermoplastic binder. In the second stage the optimization of the printing parameters within selected 3D printing software was done and standard FFF printer configuration with nozzle size 400 μm was used. In the third stage the debinding and sintering of glass structure was performed below estimated glass transition temperature (T_g).

Keywords: Composite filament production, 3D printing, FFF of Glass, Printability

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Innovative slicing strategies for additive manufacturing of bioceramic scaffolds

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ABSTRACT

Production of specialised ceramic objects by the means of additive manufacturing (AM) methods, whether using the extrusion of a ceramic paste (robocasting – RC) or the extrusion of molten polymer-ceramic composite (Fused Filament Fabrication of Ceramics - FFFC), has become extremely popular due to the ability to create complex parts with almost no special/geometrical limitations. Oftentimes, the technology used for ceramic AM was adapted from polymer-based systems, although some techniques (such as robocasting) were originally designed to work specifically with ceramic materials.
Every AM technology requires transformation of a 3D object, often characterised by edges and surfaces, into a set of 2D instructions for the manufacturing device (*slicing*). For extrusion-based methods such as FFFC or RC the workflow usually requires creation of a set of XY coordinates with given extrusion characteristics, duration of extrusion or another quantitative characteristic.
One of the limitations of FFFC is the fact that almost all software tools used in the *slicing* process naturally accounting for the employment of polymer filament as the raw material, since they were created for production of polymer-based objects. Due to the differences between polymer and composite filament, some settings commonly used for polymer AM are not favourable for ceramic 3D printing. For example, if the polymer filament exhibits so-called *oozing* behaviour (extrusion of small amounts of material even after the machine receives instruction to stop extrusion, usually between moves within the layer), the prevention of such phenomena is less straightforward for ceramic composite filament. The optimal approach to the extrusion of ceramic composites or ceramic pastes seems to be a continuous flow of material when producing the individual layer and avoiding movement of the printhead above the print layer without active extrusion. This is usually not possible using a conventional slicing software. Therefore, multiple solutions are used to achieve a higher level of control over the printing process to generate the instruction set for the AM device – some of them are just simple modifications of existing slicing software, while others allow for the use of standalone application packages specialised only for g-code generation. In this work, we discuss the development of latest trends in the ceramic slicing software with regard to utilization of such tools in the production of bioceramic scaffolds using FFFC.

Keywords: additive manufacturing, biomaterials, bioceramic.

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Influence of order-disorder transition on the thermophysical properties of $A_2B_2O_7$ high-entropy oxides

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ABSTRACT

A series of high-entropy $RE_2B_2O_7$ (RE = La, Sm, Eu, Gd, Yb, Tm, Er, Dy, Y; B = Ce, Zr and Hf) oxides were designed and synthesized via a solid-state reaction method. By tuning the atomic radius ratio r_A/r_B, these high-entropy $A_2B_2O_7$ oxides can undergo a transformation from a pyrochlore to a fluorite structure, accompanied by an order-disorder transition. The thermal conductivities of all the synthesized high entropy oxides are in the range of 1.35-1.85 $W \cdot m^{-1} \cdot K^{-1}$ at the test temperature of 1000°C, approximately half of that of oxide-yttria stabilized zirconia YSZ and lower than that of lanthanum zirconate (~1.9 $W \cdot m^{-1} \cdot K^{-1}$). The thermal expansion coefficient of all the synthesized high entropy oxides ranges from 10.5×10^{-6} K^{-1} to 11.82×10^{-6} K^{-1} exceeding that of the YSZ and single component zirconates as conventional top layer materials for thermal barrier coatings (TBCs) application. Thermophysical properties and sintering behavior are typically crucial indicators for assessing the application potential of TBCs. A dual-site multi-component tuning approach was employed to investigate how the transition from an ordered pyrochlore structure to a disordered defect fluorite structure affects the thermophysical properties and sintering behaviour. The results indicate that increasing the average ionic radius ratio (r_A/r_B) and size disorder (δ_R) enhances the sintering resistance. While doping Ce^{4+} on the B-site and reducing the ionic radius ratio (r_A/r_B) increase structural disorder, leading to reduced thermal conductivity and higher thermal expansion coefficients, the presence of Ce^{4+} compromises the sintering resistance. The findings provide a new insight into the development of high-entropy ceramics with extremely low thermal conductivities for next-generation TBCs.

Keywords: Thermal barrier coating (TBC), high-entropy oxide, thermal conductivity, thermal expansion coefficient.

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Preparation of single-phase high entropy ceramic for further modification

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ABSTRACT

High entropy ceramics (HECs) are single-phase materials consisting of five or more types of cations or anions. This is intended to give them improved properties such as thermal and chemical stability, wear resistance and mechanical properties compared to binary ceramics. HEC can also be modified and prepared as transparent and/or luminescent materials. This area of research is relatively new and under-explored.

This work aims to prepare and characterise a single-phase HEC with the zirconate structure $RE_2Zr_2O_7$ (RE stands for various rare earth elements and yttrium). The specification of zirconates is that they can crystallise in two crystal lattices: defect fluorite and pyrochlore. The cation ratio (rRE/rZr) is one of the methods used to predict the lattice type. Therefore, to cover both lattice types, five different compositions were designed using this method.

The composition Er_x:$(La_{0.7}Gd_{0.6}Y_{0.5-x}Sm_{0.1}Yb_{0.1})Zr_20_7$ corresponds to pyrochlore structure and the composition Er_x:$(La_{0.1}Gd_{0.6}Y_{0.5-x}Sm_{0.1}Yb_{0.7})Zr_20_7$ to defect fluorite structure. To investigate the effect of the type of matrix on the photoluminescence (PL), erbium was added as a dopant to both compositions in two concentrations (X = 0.01 and 0.05). For comparison $(La_{0.7}Gd_{0.6}Y_{0.5}Er_{0.1}Yb_{0.1})Zr_20_7$ with erbium incorporated directly into the HEC structure was prepared.

All samples were prepared by reaction sintering from commercially available nanopowders homogenised in water suspension. Drying was carried out in a spray dryer and the resulting powder was formed into pellets by uniaxial pressing followed by cold isostatic pressing. The organic residues were burnt out at 1000 °C for 6 hours in air. The samples were sintered both in air and in vacuum under different regimes. The effectiveness of each sintering approach was evaluated in terms of final sample density obtained by the Archimedes method and microstructure characterised by SEM. Phase composition was investigated by SEM-EDS and XRD analysis. Photoluminescence (PL) properties were measured and the effects of erbium content and matrix structure on PL were evaluated.

Keywords: $A_2Zr_2O_7$, Defect-fluorite structure, HEC, Luminescence, Pyrochlore structure.

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High-entropy ceramics with garnet structure

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ABSTRACT

High-entropy or multi-component oxides represent a new class of materials that has been widely studied in the last decade for their superior properties and functionality. However, their expansion into the optical field through the fabrication of high-entropy transparent ceramics with photoluminescent properties is in its early stages, and it is not yet well understood whether high-entropy materials have the potential for enhanced functionality in this area as well.

This study had two main objectives: (1) to prepare high-entropy ceramics with garnet structure, and (2) to study its photoluminescent properties and compare them with those of a standard doped yttrium aluminium garnet.

For this purpose, Ce-doped high-entropy garnet $(Ce_xY_{0.2-x}Yb_{0.2}La_{0.2}Gd_{0.2}Sm_{0.2})_3Al_5O_{12}$ and standard Ce-doped yttrium aluminium garnet $(Ce_xY_{1-x})_3Al_5O_{12}$ have been prepared and characterised (x = 0.005 and 0.01). Powders for consolidation were obtained by spray drying of suspensions containing a mixture of commercial nanooxide powders with colloidal suspension of SiO_2 and MgO as sintering aids. Green bodies were prepared by dry pressing followed by cold isostatic pressing. Densification was achieved by vacuum sintering.

Phase composition of the prepared samples was determined to verify the formation of a single-phase material. Density, microstructure and photoluminescence were then investigated to assess the effect of high-entropy structure on the final material characteristics.

Keywords: High-entropy ceramics; Garnet; Microstructure; Phase composition; Photoluminescence; Vacuum sintering

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SiC whiskers as a secondary phase within the structure of HEC and its effect on tribological and oxidation properties

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ABSTRACT

The presented study focused on the analysis of the influence of the addition of SiC whiskers on the tribological behavior and oxidation resistance of high-entropy (TiZrHfNbTa)C carbides. HEC-SiC_w composites were prepared using ball milling and subsequent spark plasma sintering at a temperature of 2100 °C/10 min. The amount of SiC_w in the composite varied from 1 to 10 wt. %. The resulting composites showed a high relative density exceeding 99% with homogeneous chemical composition. Tribological tests showed that all tested composites showed a stable coefficient of friction around the value of 0.3, independent of the content of SiC_w. The specific wear rate varied from 1.50×10^{-6} $mm^3/N{\cdot}m$ to 2.66×10^{-6} $mm^3/N{\cdot}m$ depending on the applied load. The obtained results indicate that the presence of the SiC_w phase in the matrix of the composite has a positive effect on the wear mechanisms. The results of the dynamic oxidation showed that with increasing SiC_w content, the rate of dynamic oxidation decreases compared to HEC-0SiC_w. The surface of the ablated samples was covered with a discontinuous oxide layer, the properties of which differed depending on the SiC_w content (thicker layers of molten metal oxide, reduced central or central zone, oxidation products in the center and at the edge). The results of this study confirmed that the addition of SiC_w to high-entropy carbides has a positive effect on their tribological and oxidation properties. The obtained results open up new possibilities for the use of these composites in applications where high demands are placed on resistance to wear and oxidation at high temperatures.

Keywords: High-entropy carbides; SiC whiskers; Oxidation properties; Friction; Wear resistance.

Composition	Weight before oxidation [mg]	Weight after oxidation [mg]	Dynamic oxidation rate [$mg{\cdot}cm^{-2}{\cdot}s^{-1}$]
HEC-0SiC_w	6379,4	6478,6	0,526
HEC-1SiC_w	6742,9	6816,4	0,390
HEC-3SiC_w	6663,2	6723,5	0,320
HEC-5SiC_w	6704,9	6753,0	0,255
HEC-10SiC_w	6676,8	6669,4	0,030

Tab. 1 Dynamic oxidation measurement on HEC samples with different SiC content (from 1 to 10 wt. %)

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In vivo assessment on calcium phosphate-based scaffolds with a selective cell/tissue ingrowth

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ABSTRACT

Highly porous bioceramic scaffolds are widely used as bone substitutes in many applications. Calcium phosphate-based bioceramics, and their doped or modified alternatives, represent a promising option for regenerative medicine because of the phase composition close to the human bones and teeth. However, the use of bioceramics is often limited to hard tissues due to the risk of potential soft tissue calcification and ectopic bone formation. A further limitation of highly porous bioceramic scaffolds is their poor mechanical stability, manifested by their tendency to break under stress. In our study, highly porous CaP-based scaffolds were prepared via freeze-casting with longitudinal and oriented pores ranging from 10 to 20 μm and a relative porosity of ~70%. The resulting scaffolds achieved a flexural strength of 10.6 ± 2.7 MPa and a compressive strength of 15.2 ± 1.9 MPa. Obtained mechanical performance together with high bioactivity, made scaffolds suitable for *in vivo* testing. The prepared scaffolds were subcutaneously implanted in rats for two distinct periods: 6 weeks and 6 months. The subsequent development of fibrous tissue and involvement of myofibroblasts, newly formed vessels, and macrophages were observed, with notable changes in spatial and temporal distribution within the implantation. The absence of calcification and/or ectopic bone formation in the surrounding soft tissue due to the narrow pore geometry indicates the opportunity to tailor scaffold behavior for soft tissue regeneration.

Keywords: β-tricalcium phosphate, bioceramics, calcium phosphates, freeze-casting, scaffold, tissue engineering.

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Hydroxyapatite-Based Microscaffolds – Their Properties and Limitations

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ABSTRACT

Hydroxyapatite ($Ca_5(PO_4)_3OH$) is the main inorganic component of human bones and teeth and its use as a material for bone implants and substitutes has been studied intensively [1]. One of the modern applications of artificially created structures in the field of orthopedics and dental surgery is the implantation of so-called scaffolds to weakened bone tissue. These scaffolds are biocompatible structures that can provide an environment where cells can attach and proliferate. To ensure the correct porosity of the material, scaffolds have in recent years started to be prepared using the 3D printing method. [2] The goal of this work was to fabricate a series of hydroxyapatite-based microscaffolds using the FDM printing method and evaluate their potential for biomedical applications by characterizing their printability, mechanical characteristics and cytotoxicity. To produce the hydroxyapatite-based microscaffolds, a twin-screw extruder was used, in which powdered pharmaceutical-grade hydroxyapatite was mixed with a PVA binder in a 1:1 ratio. To achieve desired homogeneity of the inorganic filler in the thermoplastic binder, two stage extrusion was used [3]. The resulting filament was used to prepare a series of testing microscaffolds with dimensions 5.1 x 5.1 x 0.9 mm. These microscaffolds were printed with lowered infill density to simulate the natural porosity of bone tissue. The material exhibited good printability using a commercially available 3D printer and showed no visible defects when observed by optical microscopy before and after sintering. Its cytotoxicity was analysed using MTT and LDH tests, displaying no cytotoxic effect after 48 hours in the case of the former and no negative effects on the cells' plasmic membrane using the latter method. Areas where mechanical stress would accumulate were identified using the FEM analysis.

Keywords: additive manufacturing; cytotoxicity; hydroxyapatite

Acknowledgment:

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Reinforcement Toughening of Bioactive Silicon Nitride with Beta Silicon Nitride Seeds

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ABSTRACT

This study investigates the toughening of bioactive silicon nitride ceramics by introducing beta silicon nitride seeds during the sintering process. Silicon nitride (Si_3N_4) is known for its exceptional mechanical properties, making it suitable for applications in both structural and biomedical fields. However, its fracture toughness needs improvement for specific biomedical applications like bone replacements. The research focuses on the densification and phase transformation from alpha to beta silicon nitride during spark plasma sintering at 1750°C, incorporating varying amounts of β-Si_3N_4 seeds as reinforcement. The influence of different compositions and dwell times on the microstructural evolution, grain growth, and fracture toughness of the resulting ceramics was evaluated using scanning electron microscopy and X-ray diffraction. Results showed that the addition of β-Si_3N_4 seeds improved the fracture toughness by promoting the transformation of alpha to beta phase, with elongated beta grains enhancing toughness through crack deflection and branching mechanisms. The optimal sintering conditions and reinforcement levels that led to the highest fracture toughness were identified, with smaller amounts of beta seeds providing sufficient improvement. Further investigation is required to optimize these ceramics for use in biomedical applications.

Keywords: silicon nitride, beta-Si_3N_4 seeds, spark plasma sintering, microstructure, fracture toughness.

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Hardness anisotropy of HfC and TaC ceramic grains

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The anisotropy of hardness and indentation modulus of grains of low-index crystallographic orientations ({001}, {101} and {111}), mapped by electron backscatter diffraction, were investigated by nanoindentation in polycrystalline HfC and TaC ceramics. It was revealed that the hardness anisotropy exhibited different trends for the HfC and TaC ceramics while the indentation modulus did not show detectable anisotropy. The {101} and {111} facets of HfC is found to be harder (~32 GPa) than the {001} orientation (~30 GPa) while, in the case of TaC, higher hardness corresponds to the {111} facet (~23 GPa) in comparison with the {001} and {101} orientations (~22 GPa) as shown in Figure 1. The different hardness anisotropies are attributed to the different dominant slip activation reported in the literature, providing a quick and efficient tool for the distinction between the <1-10>{110} and <1-10>{111} type active slip systems in rock salt structure transition metal carbides.

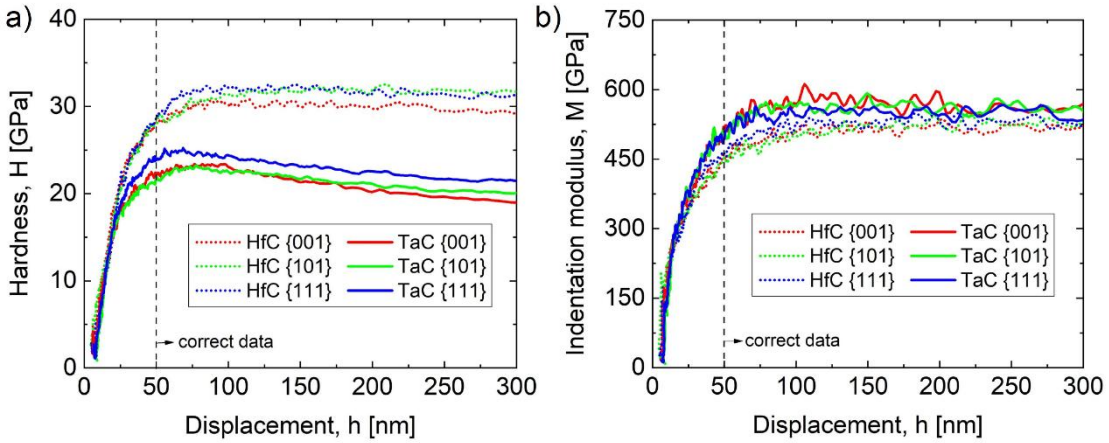

Figure 1: Typical a) hardness - and b) indentation modulus - depth curves of HfC and TaC grains measured on low index crystal facets.

Keywords: hardness anisotropy, slip systems, transition metal carbides, nanoindentation.

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Application of AI in Development of Ceramics

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ABSTRACT

As in other fields, in science too, more and more new results are being generated, the pace of which is constantly increasing. The new results not only bring positive feedback regarding the progress that society needs, but also the demands and the need to store and analyze these results. In this case, the trend of applying neural networks or otherwise known as deep learning, which uses connected points or neurons in a layered structure that resembles the human brain, began decades ago in order for computers to learn from their mistakes and constantly improve.
Large databases with various data are becoming overwhelming and the efficiency of their use is decreasing even with regard to the rate of generation of new data. This has led to the development of a number of powerful tools that help not only material scientists. In the scientific field of ceramic materials, AI is gaining ground only very slowly, although it could speed up several processes as well as the analysis of samples. Therefore, we set ourselves the goal of monitoring the possibility of using AI in ceramic science and thereby determining new trends in the development of ceramic materials.
Recent literature has highlighted the application of AI in ceramic science, primarily focused on modeling and predicting properties such as mechanical strength [1], ionic conductivity [2], synthesis feasibility [3], and more. By leveraging AI, researchers can expedite the development of new ceramic materials with tailored properties.

Keywords: artificial intelligence, ceramics, prediction, trends

Acknowledgment: The financial support of Slovak Grant Agency VEGA (grant No. VEGA 1/0070/22, 1/0342/21) and of the Slovak Research and Development Agency under the Contracts no. APVV-21-0173 and the support by the project Advancing University Capacity and Competence in Research, Development and Innovation ("ACCORD") ITMS2014+:313021X329, co-financed by resources of European Regional Development Fund are greatly acknowledged.

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Surface Treatments for Enhancing Early Osseointegration of Zirconia Implants

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ABSTRACT

Biological inertness of yttria-stabilized zirconia surfaces (3 mol.% of Y_20_3, hereafter called 3Y-TZP) results in a weak integration with bone tissue in the early osseointegration stage. To enhance the initial osseointegration of a zirconia implant, its surface topography can be modified through physical, chemical and/or biological techniques. In this work, three different surface treatments were applied on sintered and polished 3Y-TZP samples: acid etching (E), sandblasting (S), and a combination of sandblasting and acid etching (SE). For the acid etching, 40 % HF and its combination with 52.5 % nitric (HNO_3) were used (E1). A combination of 48 % tetra fluoroboric acid (HBF_4) with 63% nitric acid (HNO_3) and 36 % hydrochloric acid (HCl) was also tested (E2). The sandblasting was carried out with 25-177 μm corundum particles, followed by an etching treatment in the abovementioned acids. The features of the as-obtanied modified surfaces (E1, E2, S, SE1, SE2) and of polished samples (C; control) were investigated. Moreover, preliminary tests in phosphate-buffered saline (PBS) solution were conducted, including pH measurements at 0, 1, 2, 7, and 8 days (PBS alone was also studied and noted N). The preliminary test indicated minimal pH variations regardless of the surface treatment, thus enabling cytotoxicity and proliferation tests to be carried out.

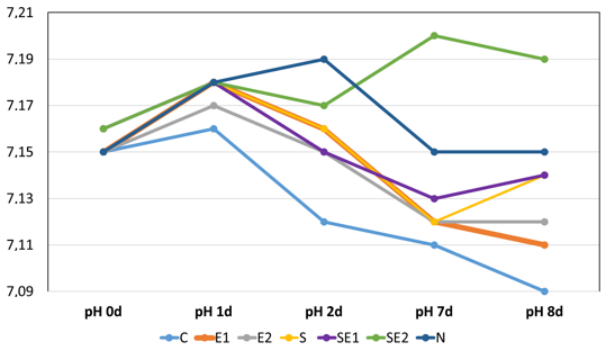

Fig. 1. pH variations observed in the preliminary test performed in PBS solution for the different modified surfaces (E1, E2, S, SE1, SE2), the control (C) and blank (N).

Keywords: 3Y-TZP, osseointegration, acid etching, sandblasting

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Zinc-Phthalocyanine Loaded Mesoporous Bioactive Glass Nanoparticles for Biomedical Applications

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ABSTRACT

Nanotechnology continues to expand its role in biomedicine by introducing novel nanoplatforms over time. Bioactive glass nanoparticles have shown promise in tissue regeneration applications for both soft and hard tissues. Their functionalization with active molecules further enhances their efficiency and broadens their range of applications. Zinc-phthalocyanines (Zn-PC) are particularly promising for developing anti-cancer therapies due to their ability to produce reactive oxygen species upon red light (660 nm) photoactivation.

In this study, we prepared Zn-PC-loaded mesoporous bioactive glass nanoparticles (MBGNPs). The MBGNPs were synthesized in the SiO_2-CaO system using a microemulsion-assisted sol-gel method [1], after which Zn-PC was loaded into the mesopores of the nanoparticles. Morphological characterization confirmed that the composite nanoparticles maintained a spherical shape without agglomeration, with particle sizes ranging between 100 and 200 nm. The optical properties of Zn-PC were preserved after loading into the MBGNPs, and the bioactivity of the MBGNPs remained intact. Cytotoxicity tests were conducted on VH-10 (human fibroblast) and MG-63 (human osteosarcoma) cell lines, both with and without red light activation. The nanoparticles showed no cytotoxic effect on either cell line without light activation. When activated with red light, cell viability decreased by 95%. The findings suggest that the synthesized nanoparticles show potential as candidates for anti-cancer applications.

Keywords: bioactive glass, photodynamic effect, mesoporous, zinc-phthalocyanine

Acknowledgment:

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Photocatalytic and Biomedical TiO_2 Nanostructures via Green Electrochemical Processing in Deep Eutectic Solvents

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ABSTRACT

The formation of TiO_2 layers on Ti and Ti alloys through anodic electrochemical processing has been demonstrated as a promising route to generate highly developed surfaces with functional applications. This study introduces an eco-friendly approach using deep eutectic solvents (DESs) containing choline chloride (vitamin B4) to synthesize micro and nanotextured TiO_2 layers, specifically focusing on photocatalytic and biomedical applications. DESs are advantageous as sustainable alternatives to conventional solvents due to their non-toxic, biodegradable, and cost-effective nature, making them ideal for green chemistry processes [1].

The electrochemical processing of Ti and Ti-alloys in DES facilitates the formation of well-developed TiO_2 nanotubes and microstructured oxide layers (Fig. 1) [1, 2]. The obtained nanostructures exhibit an enhanced photocatalytic performance. The TiO_2 nanotubes synthesized in this manner offer substantial potential for environmental applications, such as the degradation of organic pollutants under UV and visible light and catalytic HER, given the tailored band gap engineering achieved in this study.

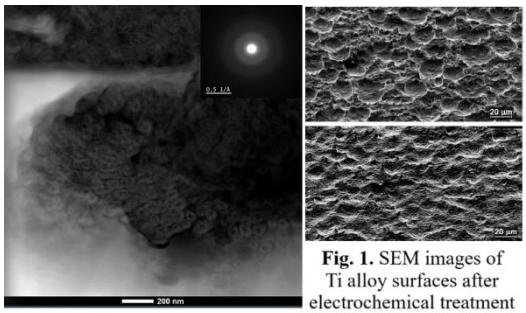

Fig. 1. SEM images of Ti alloy surfaces after electrochemical treatment in DESs.

Further work will focus on the functionalization of TiO_2 nanotubes via decoration with noble metal nanoparticles, as well as composite nanoparticles containing phosphides, sulfides, and nitrides of transition metals. These modifications are pursued as part of a band gap engineering approach aimed at enhancing the optical absorption properties of TiO_2 and optimizing its photocatalytic efficiency under a broader spectrum of light. The incorporation of noble metals such as platinum (Pt) into the TiO_2 nanotube array enables localized surface plasmon resonance (LSPR), which not only enhances the visible light response but also contributes to improved electron-hole separation efficiency. In addition to their photocatalytic potential, the tailored TiO_2 layers developed in this work demonstrate promising applications in the biomedical field. The micro and nanostructured TiO_2 surfaces provide a high degree of bioactivity, which is favorable for biomedical implants. Such nanostructured surfaces are characterized by enhanced cell adhesion and proliferation, offering potential for use in bone implants and other biomedical devices where surface bioactivity is crucial. Moreover, the eco-friendly synthesis method aligns well with the increasing demand for sustainable materials and processes in biomedical device manufacturing. The results of this study indicate that the electrochemical processing of Ti and Ti-alloys in DES is a viable and sustainable pathway for the fabrication of TiO_2 layers with versatile functional properties.

Keywords: Band gap engineering; biomedical applications; deep eutectic solvents; electrochemical processing; photocatalysis; titanium dioxide.

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Antimicrobial properties as an added value of Ag-ZnO thin films primarily designed for photocatalytic applications

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ABSTRACT

Ag-doped ZnO (ZnOAgx) thin films with varying Ag content (x = 1-10 mol%) were synthesised using a modified dip-coating sol-gel technique. All films exhibited a transmittance > 87% in the visible region of the solar spectrum. The wurzite hexagonal crystal structure of the ZnO films was preserved after Ag doping, as confirmed by the XRD analysis. The optimal photocatalytic activity was observed for the ZnOAg3 thin film with almost 100% dye degradation after 300 min irradiation, attributed to the optimal balance of surface defects. Photoluminescence spectra showed reduced electron-hole recombination in ZnOAg3 compared to ZnOAg0, enhancing the photocatalytic effect. The plausible mechanism for the enhanced photocatalytic activity is linked to the formation of a new Fermi level due to Ag incorporation, which act as an electron trap, effectively generating highly reactive oxygen species responsible for dye degradation. Reusability tests demonstrated that Ag-doped ZnO films retained their photocatalytic activity after 24 h of solar simulation exposure, indicating excellent stability for long-term use.

The addition of Ag nanoparticles also contributed to antibacterial properties of the thin films. Bacterial growth assessed by turbidity measurement showed a significant influence on adhesion and further colonisation. Reduction in the quantity of *E.coli* bacteria was ≥ 74% on all Ag-doped thin films. The level of Ag doping in tested thin films did not have any visible influence and there were no significant differences between tested samples. On the contrary, the silver content influenced Gram-positive *S. aureus* bacteria adherence to surfaces. The layers with the silver Ag1 and Ag5 enriched with silver inhibited the adherence of *S. aureus* by 26%. Samples Ag7 and Ag10 showed an even higher inhibition effect, where *S. aureus* colonised the surface 74% less than the control. An opposite trend was observed in the Ag3 thin film, where the number of *S. aureus* bacteria increased significantly and was 87% higher than in the control group. A viable cell count allows us to determine actively growing and dividing bacteria in the samples. *E. coli* bacteria visibly reduced the growth of colonies compared to the control on all thin film samples. *S. aureus* adheres and grows on the samples in higher amounts than *E. coli* however, reduction compared to control was observed.

Restriction or complete prevention of colonization may consist of inhibition of adherence itself or elimination of already adhered microorganisms. Various factors such as physicochemical properties, environmental conditions, and surface morphology influence bacterial colonisation. The actual mechanism of action must also be considered, as the mechanism of action of Ag ions is diverse and will be different for different types of microorganisms. A better understanding of the mechanisms of action requires further experiments.

The study indicates that Ag-doped ZnO thin films are promising candidates as multifunctional coatings for applications requiring both photocatalytic and antibacterial properties. They could find possible applications in places such as hospitals, food processing units, clean rooms, public transportation etc.

Keywords: Ag-doped ZnO thin films; antibacterial properties; photocatalytic activity;

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Development and characterisation of novel reactively sintered high-entropy diboride ceramic composites reinforced with SiC

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ABSTRACT

In recent years, high-entropy transition metal diborides have received attention for their potential applications in extreme environments due to their improved elevated temperature resistance, unique mechanical properties, thermal stability, and oxidation resistance compared to individual transition metal borides. A detailed systematic study investigates the influence of the sintering parameters on microstructure development and basic mechanical properties of (Hf-Ta-Zr-Nb-Ti)B_2-SiC high-entropy diboride ceramics, synthesized by reactive SPS technology. Composites were produced based on in-situ reactions and solid solution during the densification process of equimolar HfC, TaC, ZrC, NbC, and TiC, along with the corresponding amounts of B_4C and Si. The reactive sintering conditions were modified, the temperature varied from 1800 to 2100 °C, and dwell time from 5 to 20 min. Microstructural characterisation was performed by scanning electron and transmission electron microscopy. Basic mechanical properties, such as hardness, fracture toughness, bending strength, and elastic modulus were measured.

The commercially available powders, including HfC (99.5%), TaC (99.5%), ZrC (99.5%), NbC (99%), TiC (99.5%), Si (99.5%) supplied by Alfa Aesar and B_4C (>99%) from Höganäs, were used to manufacture high-entropy composites. Carbide powders were weighted in equimolar proportions in a glove box and the corresponding amount of B_4C and Si was added. The milled powder was loaded in a graphite die and consolidated using a reactive approach in SPS equipment. The samples were heated up to sintering temperature at a heating rate of 100 °C/min in a vacuum under a minimal uniaxial pressure of 7 MPa. Subsequently, for 2 min, Ar was added into the furnace chamber, and at the same time, the applied pressure was continuously increased to 70 MPa. The apparent density of the samples was measured by the Archimedes method in water. Specimens for microstructure observation and mechanical investigation were prepared by a routine ceramographic procedure they were cut, ground, and polished to a 0.1 μm finish. The microstructural characterisation was determined by SEM and TEM microscopes, phase analysis by XRD. Hardness was determined by Vickers indentation at 1 and 10 kg. The indentation toughness was calculated from the Anstis equation, and standardised CNB test was also performed for the verification of selected results. Bending strength values were evaluated in a three-point bending setup. Elastic modulus was measured by the resonant frequency method.

The combination of in-situ reaction and SPS resulted in the prepared high-entropy ceramics exhibiting significant densification and exceptional values of fracture toughness and bending strength. The relationship between microstructural development and basic mechanical properties has an important role in the further development of these perspective materials.

Keywords: ceramic composites; reactive sintering; reinforcement; silicon carbide

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Change in photoluminescence properties due to high entropy structure

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ABSTRACT

High entropy ceramics and the study of their properties have become a very popular topic in the field of materials science. Their compositional and structural diversity makes them potential structural and functional materials for a wide range of applications due to their suspected superior properties such as hardness and strength, resistance to corrosion and high temperature oxidation, thermal conductivity, stability and biocompatibility. Recently, there has also been a growing interest in the optical properties of these materials. Enhanced photoluminescence intensity associated with high entropy structure has recently been reported for samarium-doped high entropy perovskite oxide ceramics [1], halide perovskite powders [2] and transparent Nd-doped transparent fluoride ceramics [3].

However, the cited works only marginally address the issue. To verify and explain a possible positive high entropy effect on photoluminescence (PL) properties, thorough studies on different types of phosphors should be performed. In the present work, different erbium-doped powders with a garnet structure were synthesised to observe the influence of the matrix on the photoluminescence properties. Nanopowders with the compositions of $Er_{0.03}Y_{2.97}Al_5O_{12}$, $Er_{0.03}Y_{0.97}YbLuAl_5O_{12}$ and $Er_{0.03}Y_{0.57}Yb_{0.6}Lu_{0.6}Gd_{0.6}Sm_{0.6}Al_5O_{12}$ were prepared by combustion synthesis. After calcination at 1600°C, the monophase garnet structure was confirmed by XRD.

The photoluminescence (PL) intensity reached maximum in the case of Er-doped YAG and decreased with the addition of other elements into the structure. However, the presence of Yb in the structure resulted in an intense up-conversion emission in the red spectral range. On the other hand, the Sm content probably caused a luminescence quenching, both down- and up-conversion PL. In the following experiments Sm thus will be replaced by another element.

In conclusion, the positive effect of the high entropy structure on the PL properties is not universal; the influence of the elements used to create the high entropy structure seems to be crucial.

Keywords: garnet, high-entropy oxides, photoluminescence

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Strategy for preparation of high entropy ceramic materials with photoluminescence properties for photonic applications

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ABSTRACT

The concept of high-entropy ceramic materials (HEC) was for the first time proposed and investigated by Rost et al. [1] in 2015. However, for possible applications of HEC in photonics, the transparency of the material is important. This in combination with the high strength, corrosion and heat resistance of the material in the form of transparent ceramics, optical transmittance in a wide range of wavelengths, flexibility of doping predicts a great application potential of high-entropy oxides (HEO) [2]. Only a very limited number of papers dealing with the preparation and optical properties (transmission and luminescence (PL)) of high-entropy transparent ceramics (HETC) have been published so far [2, 3].
G. Zhang et al. [2] specified three HEO groups with potential for optical applications: $A_2B_2O_7$ ceramics with a defective fluorite and/or ordered pyrochlore structure, $A_3B_5O_{12}$ ceramics with a garnet structure, and X_2O_3 sesquioxide ceramics, which can easily incorporate various optically active ions (usually RE ions). The high-entropy systems thus provide great variability in composition. However, a systematic study of the effect of HETC composition (influence of environment on the absorption/emission properties of the optically active elements) and concentration of optically active elements on the photoluminescence (PL) properties of HETC is still lacking. Moreover, the composition of high-entropy systems is usually proposed as "equimolar". This may not be a big problem in the case of absorption properties, but in the case of luminescence a high concentration of PL active element in the matrix often leads to quenching of the luminescence due to so called concentration quenching (non-radiative transitions, re-absorption, cross-relaxation, energy transfer, etc.) In the present work we tried to address this issue in the proposed compositions based on the $A_2Zr_2O_7$ system (A^{3+} = PL inactive RE^{3+} ions in visible spectral range) doped with PL active RE^{3+} ions (e.g. Eu^{3+}, Er^{3+}) studied by photoluminescence steady-state and time-resolved spectroscopy.

Keywords: high-entropy oxides, $A_2Zr_2O_7$, pyrochlore/fluorite structure, luminescence

Acknowledgment: The authors gratefully acknowledge the financial support from the Slovak Grant Agency of the Ministry of Education VEGA 1/0476/22. This work also has received funding from the Horizon Europe research and innovation programme GlaCerHub under grant agreement No. 101087154.

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Effect of alumina or zirconia particles on the performance of lead-free BCZT piezoceramics

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ABSTRACT

The barium titanate derivative $Ba_{0.85}Ca_{0.15}Zr_{0.1}T_{i0.9}O_3$ (BCZT) offers high dielectric and piezoelectric performance but has poor mechanical properties. Ceramic composite materials combining BCZT with tougher Al_2O_3 or ZrO_2 could be the solution to the inherent brittleness of electroceramics. This work focuses on BCZT with 1–5 vol.% addition of reinforcing phase dispersed in the microstructure. While hardness was improved in all composites, especially in ZrO_2-reinforced BCZT, toughness was positively affected only by Al_2O_3. The chemical reactivity of BCZT during sintering resulted in the formation of new barium aluminate phases at the grain boundaries and possibly also within the grains, which affected the electrical properties of the composites. The addition of zirconia resulted in the formation of $BaZrO_3$ or $Ba(Zr,Ti)O_3$, which is a natural part of the BCZT solid solution and shifts the phase composition towards relaxor behaviour. ZrO_2-reinforced composites exhibited higher permittivity but lower ferroelectric properties, accompanied by a substantial Curie temperature decrease.

Keywords: Alumina; Barium calcium zirconium titanate; Lead-free piezoceramics; Particle composite; Zirconia

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Structure-Properties Relationship and Effect of Cation Defects in A-Site Modified $(Ba_{0.8}Ca_{0.2}Ti_{1-x})O_3$

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ABSTRACT

Ferroelectric materials with perovskite (ABO_3) structure have a long history and play a key role in electronic devices. The role of oxide perovskites is fascinating and technologically very important in electronic circuits in the form of capacitors, ferroelectric random-access memories, and energy storage applications. $BaTiO_3$ (BT) was the first discovered lead-free ferroelectric perovskite material that had the highest room temperature (RT) relative permittivity value $\varepsilon_r \sim 2000$ - 3000 with a modest curie temperature, $T_c \sim 130$ ℃. At RT, BT shows a tetragonal perovskite structure and ferroelectric nature. The phase transition temperature is the main hindrance in practical applications and can be enhanced by doping or substitution in perovskite materials. In perovskite structure, the dopant can be substituted at the A-site and/or B-site of the host with a suitable dopant [1-2]
The defect chemistry of the amphoteric Ca^{2+} dopant in $BaTiO_3$ is a controversial issue related to their site occupancy, solubility limit, and its impact on properties. In the present research work, the effect of self-induce Ti^{4+} vacancies was investigated on the structure, microstructure, dielectric and ferroelectric properties of $Ba_{0.8}Ca_{0.2}Ti_{1-x}O_3$ synthesized via solid state route. The X-ray diffraction (XRD) pattern and Raman spectra confirm tetragonal symmetry. The scanning electron microscope (SEM) images shows a decrease in grain size with induce oxygen vacancies. Electron paramagnetic resonance spectroscopy (EPR) analysis confirms the presence of Vaccancies as the gyromagnetic g-value ~ 1.995 associated with it. Temperature-dependent relative permittivity ε_r and dielectric tan loss δ, were measured in the frequency range from 1 kHz – 1 MHz. The sample at $x = 0.005$ had a maximum $\varepsilon_r \sim 8087$ at its Curie temperature T_c, along with a low tan $\delta \sim 0.009$. An increase in the W_{rec} and efficiency was observed as sample $x = 0.05$, had a W_{rec}, of 0.352 J/cm^3 and 80 % efficiency respectively. The band gap energy (E_g) reveals an increasing trend in the indirect band gap value from 3.03 to 3.10 eV. Structural transition occurs with oxygen vacancies and it greatly affects the ferroelectric properties as the sample transform from normal to relaxor ferroelectric material along with a negligible value of P_r, low hysteresis loss, and high W_{rec} which received attention as a high energy storage capacitor applications.

Keywords: $BaTiO_3$, Dielectric Properties, Ferroelectric Properties, oxygen vacancies

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NUV/Blue mechanoluminescence of Bi^{3+}-doped germanate olivine compound

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ABSTRACT

Mechanoluminescence (ML) refers to a phenomenon in which materials exhibit the emission of light as a response to various mechanical stimuli, including friction, tension, compression, impact, bending, and even ultrasound. In the last twenty years, there has been a notable increase in research efforts dedicated to the development of ML materials across the spectral range from ultraviolet (UV) to near-infrared (NIR). This heightened focus arises from the broad spectrum of potential applications for these materials, including stress sensing, photogenetics, anti-counterfeiting, and biological imaging [1-3]. Most of these ML materials mostly produce light in the visible range; nevertheless, the quantity of developed UV-emitting ML compounds is still comparatively limited.

In this context, an olivine compound $NaYGeO_4$ doped with Bi^{3+} ions was synthesized using a conventional solid-state reaction route in ambient air conditions. The crystal structure and optical properties including ML, persistent photoluminescence (pPL) and photoluminescence of the produced phosphor were systematically studied. The prepared ML material has considerable promise in the domains of stress sensing, anti-counterfeiting, and antibacterial applications.

Keywords: Bi^{3+}, Germanate, Mechanoluminescence, NUV/Blue Phosphor.

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SiC ceramics with high thermal conductivity

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ABSTRACT

Fully dense (t. d. > 99 %) silicon carbide ceramics without any sintering additives were successfully prepared by combination of freeze granulation of silicon carbide powder, annealing of granulated powders and subsequent rapid hot pressing at 1900°C with dwell time from 5 to 80 minutes. Specific heat capacity, thermal diffusivity and thermal conductivity of prepared materials considering the ratio of SiC polytypes was investigated. Different ratio of alpha and beta silicon carbide has been achieved by adjusting dwell time during sintering. Thermal diffusivity increased from 47.3 to 68.4 mm^2/s as a content of α-SiC increases from 63 to 94 %. Specific heat capacity of SiC materials increase from 0.63 up to 0.75 J/g.K at RT up to range from 1.05 up to 1.37 J/g.K at 500 °C, however there were no clear dependence between specific heat capacity and α/β content in SiC. The highest thermal conductivity (λ=165 W/m.K) among the SiC ceramics sintered at temperatures ≤ 1900°C was achieved for additive-free SiC sintered at 1900°C under vacuum for 80 minutes.

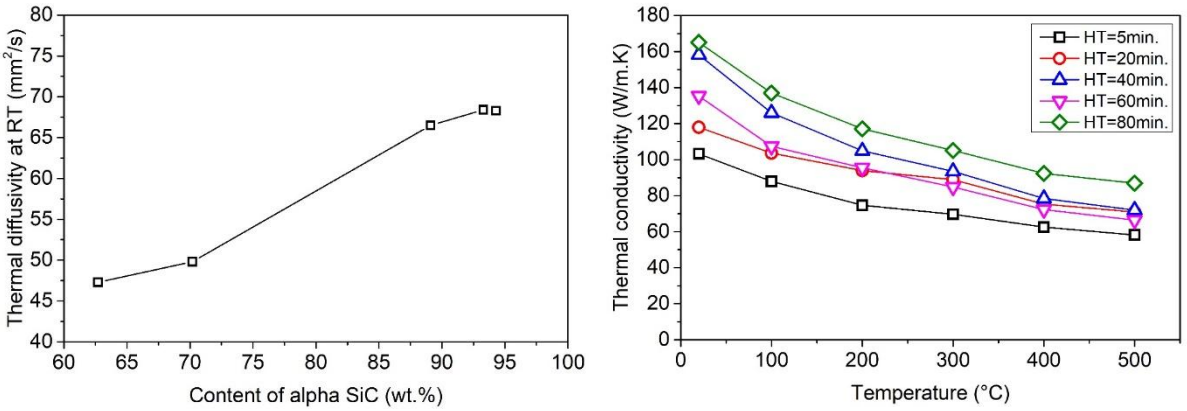

Fig. 1. Effect α-SiC content on thermal diffusivity of SiC at RT and thermal conductivity from RT up to 500°C for SiC ceramics with different sintering holding time.

Keywords: additive-free, rapid hot-press, silicon carbide, thermal conductivity, thermal diffusivity.

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Preparation and investigation of hot corrosion, CMAS, and thermal shock behaviour of double-layer YSZ/LC+YSZ thermal barrier coatings

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ABSTRACT

In this study, new double-layer YSZ/$La_2Ce_2O_7$ (LC)+YSZ coatings were developed using air plasma spraying (APS). The prepared coatings had a relatively smooth surface with melted and partially melted areas. Their resistance to hot corrosion, CaO-MgO-Al_2O_3-SiO_2 (CMAS) infiltration, and thermal shock were examined. YSZ was added to the upper layer to enhance the properties of lanthanum cerate ($La_2Ce_2O_7$, LC). During the hot corrosion tests, the corrosion salt reacted with the upper layer, leading to the identification of the CeO_2 phase and new corrosion products. The main phase identified was $LaVO_4$; the secondary phases were $CeVO_4$ and YVO_4. Additionally, scanning electron microscopy (SEM) confirmed the formation of new, cuboidal-shaped corrosion products. The infiltration of CMAS resulted in the formation of additional new products: $Ca_4Mg_xAl_4Si_{(6-x-\gamma)}O_{14}$ and $Ca_{2.8}(La_xCe_{1-x})_{.6}(SiO_4)O_{6-4x,}$ with SEM showing CMAS infiltration through the upper layer in the form of islands. The thermal shock resistance tests indicated that the upper layer gradually peeled off, with the coating surviving 67 cycles. Possible failure mechanisms were identified, with failure attributed to the spallation of the upper layer from the surface layer by layer. After all tests, the top layer showed partial spalling and delamination, mainly due to the reaction of corrosive salt or CMAS with the top layer, resulting in changes in composition, crack formation, and the separation of part of the upper layer. Peeling of the upper layer through mainly horizontal cracks was observed after hot corrosion, CMAS, and thermal shocks. The NiCrAlY bond coat and YSZ interlayer remained undamaged.

Keywords: CMAS corrosion, hot corrosion, TBCs, thermal shock resistance

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Impact of Mg Doping on Crystallization Behavior of Aluminosilicate Glasses

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ABSTRACT

Glass-ceramics are a distinguished class of materials where controlled-size crystalline particles are dispersed/embedded in an amorphous matrix. The amorphous-crystalline matrix provides distinct physiochemical properties when compared to its fully amorphous/glassy or crystalline/ceramic counterparts. The properties of glass-ceramics can be adjusted by controlling the crystal phase concentration and morphology in the amorphous matrix. Magnesium aluminosilicate (MAS) is an important glass-ceramic material widely used in advanced engineering applications such as ultrahigh vacuum, high temperature, and high voltage [1]. Owning to its high mechanical and thermal stability, high chemical stability, and, also, magnesium ions therapeutic nature, magnesium aluminosilicate glass ceramics are of particular interest to applications such as bone cements, bone grafts, implant coatings, tooth filling materials, and even pharmaceutical packaging material applications [2], [3]. Glass composition and structure, as well as heat treatment (HT), are key parameters in modifying the properties of MAS glass ceramics. Therefore, it is essential to study the impact of HT on crystallization behavior of MAS glass for tailoring the desired properties.
In the present study, we have synthesized the simplified version of commercial glass-ceramics SCHOTT CERAN® with the replacement of Li_2O to MgO (from 0 to 25 wt% (35.4 mol%)) and studied the structural evolution of magnesium aluminosilicate glasses (MAS) as a function of temperature by HT-Raman and HT-XRD in addition to other techniques such as SEM and XPS. The substitution of Li with Mg not only reduces the costs but also affects its physiochemical properties. Up to 20 wt% (29 mol%), quenched samples were obtained amorphous in nature. However, at 25 wt% (35.4 mol%) MgO content, the quenched sample contained a Mg-rich ceramic phases (Mg_2SiO_4 and $Na_3MgAlSi_2O_8$) and a Mg-poor glassy phase. The quenched glasses showed an increase of Tg with an increase of MgO content. The crystallization temperature (Tc) decreased with MgO addition. As expected from Tg and Tc behavior, the onset of sintering temperature increased with Mg content. However, the shrinkage temperature window (from onset of sintering to fully densification) decreased. The obtained results facilitate in designing the sintering regime and tailoring the final properties of MAS glass-ceramics.

Keywords: Crystallization of MAS, Glass-ceramics, HT-Raman, HT-XRD, MAS glass, SCHOTT CERAN®

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The effect of Stoichiometry on Mechanical and Electrical Properties of NbMoTaW-$(CN)_x$ Coatings

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ABSTRACT

The work focuses on the effect of stoichiometry in NbMoTaW-$(CN)_x$ coatings deposited by reactive DC magnetron co-sputtering from a NbMoTaW composite and carbon targets and nitrogen on their structure, composition, hardness, elastic modulus and superconductivity. The coating stoichiometry has been controlled using three different power levels on the carbon target while keeping the power on NbMoTaW target constant and nitrogen flow from 0 sccm up to 5 sccm. The chemical composition of the coatings has been determined by time-of-flight elastic recoil detection analysis (ToF ERDA) and semi-quantitative EDS/SEM. These measurements were corroborated with the results of phase analysis by X-Ray diffraction, nanoindentation and the measurements of T_c – critical temperature when superconductivity has been achieved.

The increase of power on carbon target from 500 W to 700 W in 100 W steps without nitrogen resulted in the increase of carbon concentration in the coatings from 42.0 at% up to only 44.8 at % which means that the stoichiometric ratio was not achieved. However, substantial changes in X-ray diffractograms indicated that although fcc structure corresponding to TaC or NbC remained, carbon content increase caused changes in texture and crystallite size: relatively well defined (111) texture at 500W on C target was gradually lost, peak intensities were reduced and their FWHM increased suggesting reduction in crystallite size and amorphization. In contrary, tthe additions of nitrogen was more effective – 2 sccm and 5 sccm N_2 flows caused the presence of 15.6 at% and 32.9 at% of nitrogen in the coatings. Nitrogen addition affected mostly preferred orientations. The addition of 2 sccm C_2H_2 into Ar + 5 sccm N_2 atmosphere resulted in the increase of carbon content up to 60.2 at.%. Moreover, more than 5.6 at% of hydrogen originating from the hydrocarbon groups was detected besides 17.5 at % of nitrogen and amorphization without any texture.

The mechanical properties as well as T_c were strongly affected by coating composition and structure. The hardness values were in the range below 35 GPa and a degradation was observed in the presence of excessive amount of carbon and hydrogen after addition of acetylene. The corresponding T_c values were below 10 K and they were only weakly affected by carbon concentration.

Keywords: DC magnetron sputtering, nanoindentation, stoichiometry, superconductivity, TiNbMoTa-carbide coatings.

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Temperature dependent transformation of rare earth modified smectites: Probing of the spectroscopic responses

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ABSTRACT

The behavior of the selected smectites was systematically analyzed both before and after modification with the rare earth elements, and their subsequent heat treatment to temperatures corresponding to dehydration (400 °C), dehydroxylation (800 °C), and the formation of high-temperature phases (1200 °C). The temperature-dependent changes in the samples were examined using thermogravimetric analysis, powder X-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, terahertz time-domain spectroscopy, and UV-VIS-NIR fluorescence spectroscopy. Phase transformations were observed immediately after dehydroxylation, with new phases beginning to form at 800 °C, where the primary diffractions of forsterite (Mg_2SiO_4) and/or enstatite ($Mg_2Si_2O_6$) ceramics were detected. Heating to 1200 °C allowed the identification of erbium silicate ($Er_2Si_2O_7$) and/or ytterbium silicate ($Yb_2Si_2O_7$) by X-ray diffraction, which are important phases for applications in electromagnetic radiation up-conversion or photonic devices, such as optical waveguide amplifiers.
Interestingly, the energy dispersive spectroscopy identified growth of erbium/ytterbium silicate phases with crystal size ranging from ~0.1 μm up to 5.0 μm for samples heated to 1200 °C. THz-TDS spectroscopy also revealed the formation of new products in the far-infrared region, characterized by an increase in the frequency-dependent refractive index and a decrease in the absorption coefficient compared to the unmodified clays. The synthesized ceramic materials exhibited characteristic emission bands in the green (540 nm) and red (670 nm) regions when irradiated by a 980 nm laser. The red/green (R/G) emission decreased from 4.1 observed for hectorite modified with Er and heated at 1200 °C sample to 2.2 as the red emission dominate over the green emission in all recorded UC spectra. These findings suggest that the functionalized ceramic structures derived from modified smectites are suitable for processing using additive manufacturing technologies, particularly those based on composite photopolymerization.

Keywords: smectites, cation exchange, rare earth elements, phase transformation, phosphors, up-conversion.

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Effect of sintering conditions on microstructure evolution of ultrahigh temperature monocarbides

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ABSTRACT

This study investigates the effect of sintering conditions on microstructure evolution of ultrahigh temperature carbides. All of the six Group IV and V transitional metal carbides (TMCs), namely TiC, ZrC, HfC, VC, NbC and TaC, were processed from commercially available carbide powders using a spark plasma sintering (SPS) machine. The rationale for the selection of only these six carbides is due to the highest thermal stability of their oxides within the Group IV-VI TMCs, known as ultra-high temperature ceramics.
Sintered materials were prepared using ball milling (4h) and then consolidated via SPS at 2 100 °C during 10 or 20 minutes at 70 MPa in argon atmosphere. Both the raw powders and sintered samples were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) with energy-dispersive x-ray spectroscopy (EDS) to analyze the microstructure and phase composition.
Monocarbides achieved relative density over 98 %, with homogeneous chemical composition and grain sizes from 2 μm to 5 μm, while TaC achieved the highest porosity. Longer sintering of 20 minutes has no significant influence on grain growth of carbides. The phase analysis confirmed the existence of monocarbides with lower content (< 2 wt.%) of oxidic phases ZrO_2, and below 0.5 wt.% of TiO_2 and HfO_2 in the case of TiC and HfC carbides.

Keywords: UHTC monocarbides, sintering, microstructure, phase composition

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